

## MEASUREMENT OF THE ADSORPTION AND CRACKING OF MODEL COMPOUNDS OVER PROCESSED OIL SHALE PARTICLES

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**Keywords:** Cracking reactions, adsorption-desorption, oil shale.

A parallel reactor system has been constructed to monitor adsorption, desorption, and/or cracking/coking of vapor phase model compounds over solid substrates at elevated temperatures. In this study, selected hydrocarbons ranging from benzene to n-decane were passed across pyrolyzed, gasified, or combusted oil shale particles at temperatures between 270 °C and 650 °C. A vapor phase hydrocarbon, Ar tracer gas, and N<sub>2</sub> carrier are combined and routed through a heated switching valve to a sand-packed tube reactor positioned within a tube furnace. A parallel line routes N<sub>2</sub> gas through a second tube reactor packed with substrate. After exiting the tube reactors, the two lines are combined and sampled by a heated capillary connected to the inlet of a quadrupole mass spectrometer (QMS). A typical run entails establishing a QMS baseline with the model compound passing through the sand-packed reactor, switching the valve so the model compound passes through the substrate bed, then returning to the sand-packed reactor to re-establish the QMS baseline.

**Introduction.** The utilization of fluidized bed retorting technology for the processing of the Eastern US oil shale deposits has been under investigation at the CAER since about 1982. Development has progressed from small independent grams/hours pyrolysis, combustion, and gasification reactors, through operation of an integrated, 3-stage, 5-lb/hr unit and currently, construction of an integrated 50-lb/hr pilot plant representing the most recent effort to provide proof of concept for KENTORT II. KENTORT II is designed to maximize oil and gas production and to fully utilize the carbon contained in Eastern US oil shales without resorting to exotic or high pressure atmospheres<sup>1,2</sup> and to do so in an environmentally acceptable manner.

In the KENTORT II reactor, pyrolysis heat is provided by recycling hot gasified or combusted particles to the pyrolysis zone. Thus, of particular interest are those reactions that can be attributed to the recycling of hot solids and which impact oil yield, i.e., cracking and coking reactions. Within limits, the detrimental effect of recycling hot solids to the retort can be minimized by varying the relative proportion of gasified versus combusted particles or by selecting the optimum recycle rate/particle temperature, i.e., fewer high temperature vs. more low temperature particles.

A previous study<sup>3-4</sup> focused on the kinetics of shale oil coking as a function of substrate type and temperature using gasified, combusted, and pyrolyzed shales. In a similar manner, the current study will focus on product adsorption and cracking. However, unlike the coking study which utilized freshly generated shale oil, the measurement of adsorption and cracking kinetics in the system described here dictated the use of model compounds.

**Experimental. Reactor System.** A simplified schematic of the reactor system is shown in Figure 1. High purity N<sub>2</sub> is introduced to a heated valve oven (275 °C) at 100 psig, split into parallel carrier lines and routed through a pair of metering valves. From the metering valves to the reactor, all carrier/transfer lines are constructed of 1/16" x 0.03" 304 ss.

One of the carrier lines, termed the bypass line, is routed through a switching valve, an 18" heat traced transfer line, a 48" preheater coil, and into one of the parallel tube reactors positioned in a 2"

x 15" Lindberg tube furnace. In the initial "bypass" mode, this line is routed through the substrate-packed reactor (substrate reactor).

High purity Ar is introduced at 100 psig and metered to the parallel HC carrier line just downstream from the N<sub>2</sub> metering valve. A Waters model 6000A LC pump is used to dispense the liquid hydrocarbon (HC) which first passes through a restriction coil to maintain pump back pressure (and thus constant flow), then into the valve oven where it passes through a downward spiraling volatilization/surge suppressor coil before connecting to the HC carrier line. The HC line parallels the bypass line to the reactor furnace where, in the initial valve position, it passes through the sand-packed bypass reactor.

After passing through the parallel reactors, both lines are combined and continuously sampled just inside the reactor furnace by a heated capillary connected to the inlet of a VG/Fisons Sensorlab 300D quadrupole mass spectrometer (QMS). The QMS may be operated in either a log histogram mode which monitors all mass intensities at 1-amu resolution from zero to a selected upper limit (usually just above the molecular ion of the model compound) or in a selected ion monitoring (SIM) mode which records up to 16 selected ion intensities at approximately 1 second intervals. The latter is the preferred operating mode due to a more rapid sampling rate but with the trade-off that not all ion intensities are monitored.

The tube reactors are constructed of 9" x 3/8" -o.d. (1/4" i.d.) 316 ss. One of the reactors, the bypass, is packed with 6-gm of sand while the second, the substrate reactor, is packed with 4-gm of one of the substrates listed in Table 1. Quartz wool is used to hold the solids in place. Substrates are centered in the reactor tubes with an approximate 2" void on each end. A type K thermocouple is placed into each reactor tube, 2.5" from the entrance to the bypass tube and 4" from the entry to the substrate tube. The substrate was removed following each run, crushed, and submitted for elemental analysis. The bypass sand was replaced after each 650 °C run (or when the model compound or study substrate was changed).

**Study Substrates.** The three substrates examined in this study (Table 1) originated from the CLE-003 master sample taken from Fleming County, Ky.<sup>1-3</sup> These materials represent the three types of solids present in the pyrolysis section of the KENTORT II reactor to which the vapor phase shale oil is exposed. All three substrates were prepared in a fluid-bed reactor using N<sub>2</sub>, steam, or air as the fluidizing media (Table 1). All three substrates were screened to 20 x 60 mesh. The Ottawa sand was screened to 20 x 30 mesh.

**Run Conditions and Procedure.** A nominal model compound flow of either 0.1 or 0.2-mL/min was used for all runs. A total gas flow of 150 mL/min (ambient temperature) was maintained through each reactor. This flow was comprised solely of N<sub>2</sub> in the bypass line. For the HC carrier line, Ar tracer gas flow was set to 50 mL/min; the volume of the gas phase model compound was calculated assuming ideal gas behavior; and the cumulative flow adjusted to 150 mL/min with high purity N<sub>2</sub>.

Run preparation entailed packing 4-gm of substrate to the substrate reactor and 6-gm of sand to the bypass reactor, setting the Lyndberg furnace controller to the target temperature with the reactors in place, and initiating carrier gas and model compound flow. QMS data collection was initiated following a minimum 2-minute equilibration at temperature. The substrate thermocouple reading was manually maintained within ±2 °C of the target temperature for the duration of the run. After a minimum of 100 data points were collected in the SIM mode (or at least 2 minutes in the log histogram mode), the valve was rotated so that the HC carrier passed through the substrate reactor (make-up line is simultaneously switched to the bypass reactor). Following the selected exposure time, the valve was returned to the initial position and the QMS baseline reestablished. Control runs were made by packing both the bypass and substrate reactor tubes with sand to ensure acceptable system operation.

**Data Management.** Following data collection, the QMS data files are imported to a spreadsheet where the model compound's molecular ion (and/or selected cracking product) intensity is ratioed to

the Ar intensity. These ratios are then exported to a curve-fitting software routine (Sigma Plot) where a linear equation was fitted to the data points collected in the bypass mode (before and after HC/substrate exposure). A function containing both linear and decaying exponential terms (eq. 1) was fitted to the molecular ion/Ar ratio obtained during substrate exposure:

$$\text{Eq. 1} \quad y = -a * \exp(-bt) + c * t + d$$

The difference in the integrated area between the linear and exponential equations over the substrate exposure interval represents either product loss due to cracking/coking reactions for the high temperature runs ( $\sim 500^\circ\text{C}$ ), to HC adsorption for low temperature runs ( $\sim 400^\circ\text{C}$ ), or to a combination of these at the mid temperature ( $\sim 400\text{--}500^\circ\text{C}$ ). Further, since the HC flow is known, HC loss can be expressed on an absolute basis, i.e., gms HC/gm substrate.

**RESULTS AND DISCUSSION:** A typical run sequence in which cyclohexene was passed through gasified shale at  $500^\circ\text{C}$  is shown graphically in Figure 2a. The response as plotted shows the ion intensity for the molecular ion of cyclohexene ratioed to the Ar ion intensity. Data are displayed as ratios instead of absolute intensities in order to correct for changing conditions during a run, e.g., QMS drift, pressure fluctuations, etc. The first segment represents QMS response in the initial valve position (bypass mode) in which the model compound is flowing through the sand-packed bypass bed. The second segment shows QMS response with the valve switched so that the model compound passes through the substrate reactor. The third segment shows the return to bypass mode at which time the QMS baseline is reestablished.

There is no measurable desorption in the data of Figure 2a following return to bypass suggesting that all product loss is attributable to cracking or coking losses. Evidence that this loss is due in large part to cracking reactions can be found in Figure 2b, which shows a substantial increase in the mass 42 (largely propene) to mass 82 (cyclohexene) ratio during exposure.

The high initial HC loss followed by a gradual decline to constant response was characteristic of the high temperature runs (Figure 4). Generally, substrate reactivity followed the order of gasified > combusted  $\geq$  pyrolyzed. Also, cyclic aliphatics were found to be more susceptible to induced reaction than were straight chain aliphatics with aromatics generally exhibiting the greatest stability. As of this writing, carbon analysis of the substrates is incomplete and thus product loss due to coking versus cracking cannot yet be differentiated. However, it is believed that cracking reactions (i.e., thermal cleavage with little or no coke deposition) are much more prevalent for aliphatics (particularly cyclic aliphatics) than aromatics which more likely undergo a higher proportion of coking reactions in the initial interaction. To help differentiate between cracking and coking losses, future runs are planned in which the total product stream will be combusted with the resulting  $\text{CO}_2$  and  $\text{H}_2\text{O}$  products monitored with the QMS. It is anticipated that this approach will unambiguously determine coking losses with cracking losses determined by difference.

Figure 3 shows a similar cyclohexene/Ar ion intensity plot at a lower temperature of  $300^\circ\text{C}$ . HC loss in this run is attributed solely to adsorption since 1) the QMS response during the bypass mode and the latter portion of the expose mode are equivalent and 2) the desorption curve following return to bypass is equal in magnitude to the HC loss observed in the initial stages of substrate exposure. Generally, adsorption capacity followed the order of gasified >> combusted  $\geq$  pyrolyzed shale. Adsorption was so extensive for many of the low temperature gasified shale runs that QMS response dropped off-scale resulting in a delay in data collection of up to 2 minutes in some instances.

**SUMMARY.** The reactor system described in this manuscript provides a rapid means of measuring HC reaction kinetics. The system is flexible in that direct comparisons of solid substrate reactivities may be compared over a wide temperature range with a variety of hydrocarbons. Though

not discussed, fixed gases are also amenable to adsorption/desorption studies by this technique. Future plans include: 1) examination of the liquid products and ultimate analysis of the solid substrates following exposure in order to help elucidate reaction mechanisms and differentiate between predominantly cracking versus predominantly coking reactions and 2) examining mixtures of two or more hydrocarbons to determine differential adsorption/desorption kinetics.

**Acknowledgments.** The author gratefully acknowledge the work of D. McLean, G. Thomas, and M. Moore for analytical support and S. Carter for providing the oil shale substrates and for valuable discussions. This work was supported in part by the Morgantown Energy Tech. Ctr., USDOE, under Coop. Agreement DE-FC21-90MC27286 (such support does not constitute an endorsement by the USDOE of the views expressed in this manuscript).

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Table 1. Study Substrates. Substrates dry screened to 20X60 mesh.

<u>Substrate</u>	<u>Origin</u>	<u>Reactor Load (g)</u>	<u>Preparation/comment</u>
Pyrolyzed Shale	Cleveland oil shale	4-g	530C in N <sub>2</sub> /10 min
Gasified Shale	Cleveland oil shale	4-g	800C in Steam/20 min
Combusted Shale	Cleveland oil shale	4-g	700C in air/10 min
Sand	Ottawa, Canada	6-g	20X30 mesh

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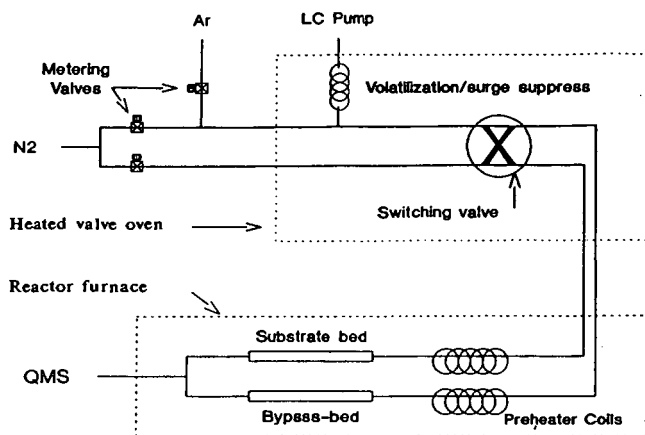


Figure 1. Adsorption/Cracking Reactor Schematic.

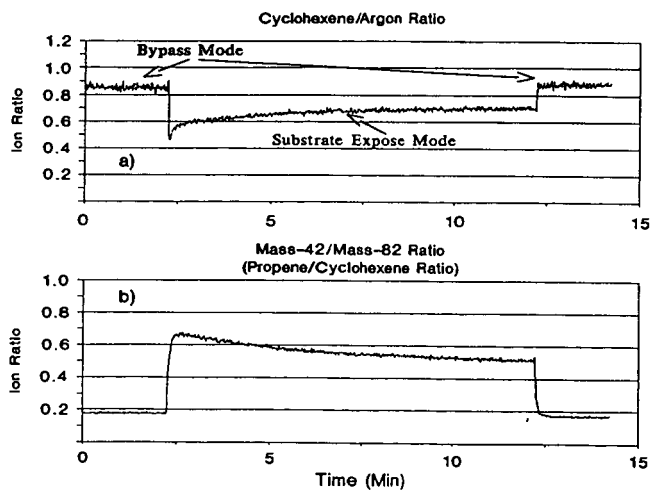
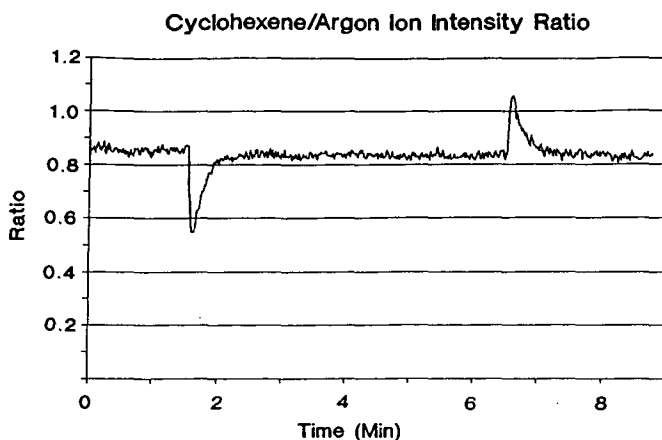
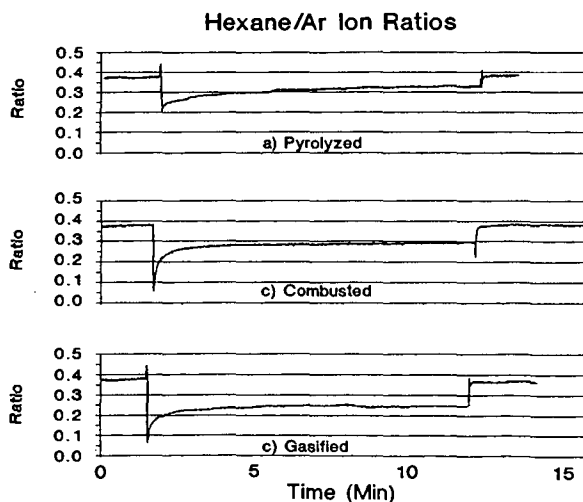


Figure 2. Gasified shale, 500 °C, 10 min exposure, ~10 vol% cyclohexene in Ar/N<sub>2</sub> carrier. a) Cyclohexene/Ar (82/20) ion ratios, b) Mass 42/mass 82 (largely propene).



**Figure 3.** Cyclohexene/Ar ion intensity during gasified shale substrate run at 300 °C, 5 minute exposure. Otherwise, same conditions as Figure 2.



**Figure 4.** Hexane/Ar ion ratios for 650 °C, 10 min exposure runs, ~10 vol% hexane in Ar/N<sub>2</sub> carrier. a) pyrolyzed b) combusted and c) gasified substrate.